Short communication

Ce$_{0.8}$Sm$_{0.2}$O$_{2-\delta}$–PrBaCo$_2$O$_{5+\delta}$ dual-phase membrane: Novel preparation and improved oxygen permeability

Ting Chen [a], Hailei Zhao [a,b,*], Zhixiang Xie [a], Jie Wang [a], Yao Lu [a], Nansheng Xu [a]

[a] School of Materials Science and Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Beijing 100083, China
[b] Beijing Key Lab of New Energy Material and Technology, Beijing 100083, China

HIGHLIGHTS

► Fiber-like PBCO phase forms percolative electronic conducting network in SDC–PBCO dual-phase membrane.
► The threshold forming percolative network can be decreased to 20 vol.% for PBCO in SDC–PBCO membrane.
► The SDC–PBCO (8/2 in vol.) dual-phase membrane exhibits high oxygen permeability.

ARTICLE INFO

ABSTRACT

Dual-phase oxygen permeation membrane has become much attractive due to its tailorable properties. On the premise of forming percolative network separately, decreasing the volume percentage of electronic conducting phase can increase the oxygen permeability of dual-phase membrane. However, the conventional ceramic route limits the decrease in threshold of the content of electronic conducting phase. In this work, a coating strategy is employed to fabricate a novel dual-phase membrane with 20 vol.% PrBaCo$_2$O$_{5+\delta}$ (PBCO) dispersing in 80 vol.% Ce$_{0.8}$Sm$_{0.2}$O$_{2-\delta}$ (SDC) matrix, where the fiber-shaped PBCO forms percolative network and provides sufficient electronic conductivity. The prepared SDC-PBCO membrane with 1 mm thickness exhibits very high oxygen permeability, 3.81×10^{-7} mol cm^{-2} s^{-1} at 940 °C, due to the high volume percentage of SDC. This preparation strategy can be applied to other dual-phase membranes to improve the oxygen permeation performance.

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1. Introduction

Oxygen permeation membranes have received considerable attention due to their potential applications in separation of oxygen from air, conversion of natural gas to syngas and oxy-fuel combustion technique for CO$_2$ capture [1]. The single phase membranes, conducting both oxygen ions and electrons in a same phase, have been extensively investigated for the high oxygen flux [2]. However, they show poor structural stability under reducing atmosphere for their weak metal–oxygen bond, preventing them from the practical applications [3]. Dual-phase membranes, consisting of electronic and ionic conducting phases, have attracted much research interest in recent years owing to the tailorable feature in chemical composition, microstructure and thus

performance [4,5]. Because the electronic conductivity of electron conducting phase is usually much higher than the ionic conductivity of oxygen ion conducting phase, the later becomes, therefore, the limiting factor for the oxygen permeation process according to Wagner equation [6]. Accordingly, in the dual-phase membrane the oxygen ion conducting phase should be as much as while the electron conducting phase as less as possible in order to achieve the maximization of oxygen permeation flux, under the premise of the two phases forming independently percolated network. With the conventional ceramic process, i.e. mixing–pressing–sintering process, the formed dual-phase membrane commonly has a structure of random packing of the particles of the two phases. For this case, Liu and Wu [7] reported that 1/3 volume fraction of randomly-distributed phase was the percolation threshold and within the range 1/3–2/3 the membrane could achieve percolation. To decrease the percolation threshold of electron conducting phase and thereby maximize the volume percentage of the ionic conducting phase in dual-phase membrane, it is required to design and prepare the dual-phase membranes with special microstructure.

* Corresponding author. School of Materials Science and Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Beijing 100083, China. Tel./fax: +86 10 82376837.
E-mail address: hlzhao@ustb.edu.cn (H. Zhao).

Recently, many efforts were devoted to develop dual-phase membranes with magnetic structure. Kim and Lin [8] attempted to achieve a special microstructure for Pt–YSZ membrane by impregnating Pt phase inside the mesoporous YSZ membrane, however, the Pt phase was difficult to form continuous path inside the porous YSZ membrane. To increase the oxygen ion conducting phase volume, Yang et al. [9] prepared a new $La_{0.15}Sr_{0.85}Ga_{0.3}Fe_{0.7}O_{3-\delta}$–$Ba_{0.5}Sr_{0.5}Fe_{0.2}Co_{0.8}O_{3-\delta}$ (LSGF–BSCF) dual-phase membrane with thin electron conducting BSCF film running along the close-packed LSGF grain boundaries via a conventional ceramic route by utilizing the liquid state feature of BSCF at sintering temperature. In our previous study, $Ce_{0.8}Sm_{0.2}O_{2-\delta}$–$PrBaCo_2O_{5+\delta}$ (SDC–PBCO) composite membrane exhibited great oxygen permeation performance due to the high electronic and ionic conductivity as well as the fast surface exchange of PBCO and the high structural stability of SDC. With conventional ceramic route, the electronic conducting phase PBCO could form percolative path only when its volume percentage was 40%, which limited the improvement on the permeation flux of the SDC–PBCO membrane. In this communication, we report a novel synthesis route to prepare a dual-phase composite with special microstructure, where the electronic conducting phase PBCO with fiber-like shape was generated and dispersed along the ionic conducting SDC particles, forming percolative channels for electronic conduction. The threshold of the electronic conducting phase was reduced to 20 vol.%. The prepared SDC–PBCO membrane demonstrated a remarkable improvement on the oxygen permeation flux.

2. Experimental

SDC powder was prepared by the surfactant-assisting method as we previously reported [10]. The PBCO precursor was prepared by a combined EDTA–citrate complexing sol–gel method [11]. Briefly, Pr_6O_{11} was dissolved in HNO_3 aqueous solution, and then stoichiometric amounts of $Ba(NO_3)_2$, $Co(NO_3)_3 \cdot 6H_2O$, EDTA and citric acid were added. After adjusting the pH value to ca. 8 with the help of $NH_3 \cdot H_2O$, the SDC powders were added and dispersed by an ultrasonic stirring for 10 min. The sol was dried at 80 °C with a rotary evaporator under reflux condition to make sure that the SDC particle was in the precursor matrix. The precalcination for 5 h
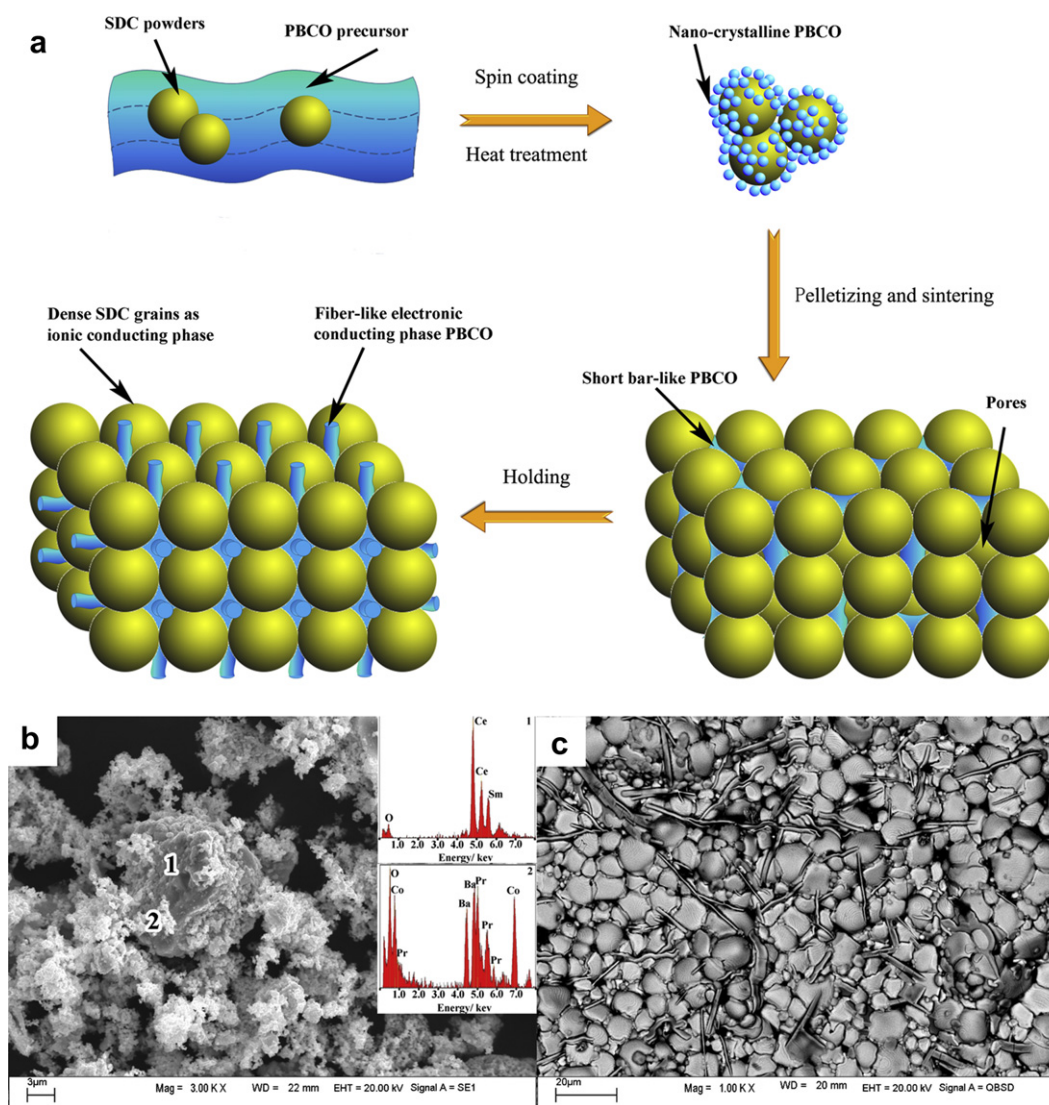
Fig. 1. (a) Schematic illustration of the novel strategy for the synthesis of SDC–PBCO membrane with fiber-like PBCO phase distributing in the matrix of SDC phase; (b) PBCO-coated SDC powders, and the insert is the EDS spectrum of the corresponding part in the coated particle; (c) back-scattered electron micrograph of the prepared SDC–PBCO (8/2) membrane. The fiber-like parts correspond to PBCO phase.

was carried out at 300 °C and the final calcinations for 4 h at 850 °C to form a nano-crystalline PBCO (20 vol.%) coating layer on the particle surface of SDC. The resulting products were compressed into disk or bars, and then sintered in air at 1150 °C for 6 h to achieve the relative densities higher than 95%.

The phase identification was studied with X-ray diffraction by Cu K$_\alpha$ radiation (XRD, Rigaku D/MAX-A). Microstructures were observed by scanning electron microscopy (SEM, LEO-1450). The electrical conductivity was measured in air by four-terminal DC method upon heating from 200 to 900 °C. The oxygen permeation experiment was performed in a vertical high-temperature gas permeation cell [12]. The oxygen permeation flux of membranes (1 mm thickness) was measured during cooling from 940 to 825 °C in an on-line gas chromatography with synthesized air (150 ml min^{-1}) as the feed gas and helium (65.8 ml min^{-1}) as the sweeping gas. Gas-tightness of membrane was examined by monitoring nitrogen to make sure the leakage was <1%.

3. Results and discussion

A schematic drawing for the preparation process of the SDC–PBCO dual-phase membrane with fiber-like electronic conducting phase PBCO dispersing inside the ionic conducting phase SDC matrix is shown in Fig. 1a. The nano-crystalline PBCO powder was coated on the surface of large SDC particles by a sol–gel spin coating method. The particle size of PBCO is much smaller than that of SDC (Fig. 1b), which is necessary to guarantee the formation of a thin layer of PBCO on the particle surface of SDC. When sintering at elevated temperature, short bar-like PBCO phase was first produced at grain boundaries. With increasing temperature and prolonging dwelling time, the fiber-like PBCO phase was formed and distributed in the matrix of SDC (Fig. 1c). The fiber-like electronic conducting phase forms the percolative network under a very low volume percentage, ensuring the maximization of the oxygen ionic conducting phase, which is believed to be beneficial to the achievement of a high oxygen permeation flux.

The XRD patterns of dual-phase membrane sintered at 1150 °C are shown in Fig. 2. All the peaks can be well indexed as fluorite SDC (JCPDS No. 75-0158) and double perovskite PBCO (JCPDS No. 53-0131) phases, which gives evidence for the good chemical compatibility between the two phases. The XRD peaks for SDC are much stronger than that for PBCO, mainly due to the high fraction of this phase in the composite.

The electrical conductivity of the prepared SDC–PBCO composite versus the temperature under air atmosphere is displayed in Fig. 3. Within the temperature range of 200–900 °C, the electrical conductivity of SDC–PBCO composite gradually increases with increasing temperature. It is well known that the electrical conductivity of SDC is much lower than that of the PBCO phase; therefore, the considerable conductivity value of the SDC–PBCO membrane suggests that the electronic conducting phase has formed the percolative channel. It is worth to note that there is a transition in the conductivity at ca. 500 °C, above that the electrical conductivity exhibits a sharp increase. This is possibly related to the lattice oxygen loss of PBCO phase. The double perovskite PBCO tends to loss lattice oxygen at around 500 °C [13], which leads to the lattice expansion and thus has the possibility to improve the contact between the fiber-like PBCO grains. The conductivity of SDC–PBCO composite reaches 5.89 S cm^{-1} at 900 °C, which is sufficient for counterbalancing the flux of oxygen permeation and making overall charge neutrality.

The oxygen permeation flux of SDC–PBCO composite at different temperatures in the range of 825–940 °C is presented in Fig. 4. In our previous work [14], the electronic conducting phase PBCO in SDC–PBCO membrane prepared by a conventional
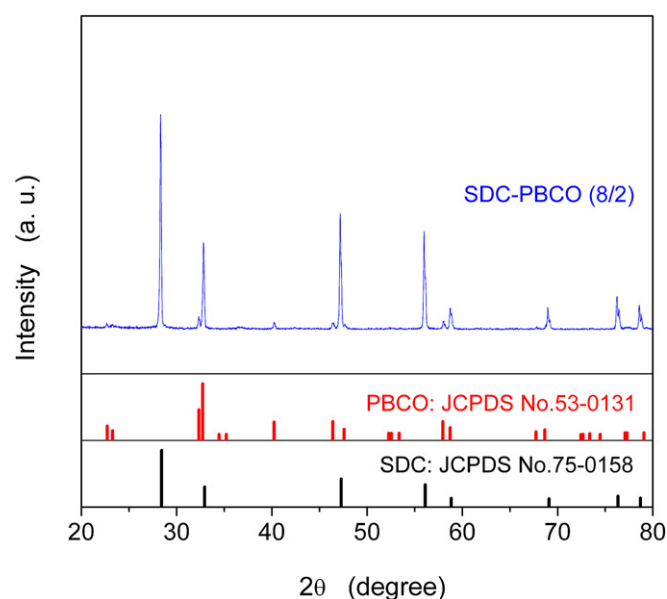
Fig. 2. XRD pattern of SDC–PBCO dual-phase membrane sintered at 1150 °C for 6 h.

ceramic route could not form percolative networks when its content below 40 vol.%, and thus the membrane SDC–PBCO (7/3) showed poor oxygen permeability. The highest oxygen permeation flux was achieved with the membrane (6/4), which is included in Fig. 4 as comparison. In this work, the composite is still electronic percolating even the ionic conducting phase is up to 80 vol.%, due to the formation of the special fiber-like electrical conducting phase. It is gratifying that SDC–PBCO (8/2) membrane demonstrates excellent permeability, as high as 3.81×10^{-7} mol cm^{-2} s^{-1} at 940 °C with 1 mm thickness, which is much higher than that of the traditional SDC–PBCO (6/4) membrane. The high oxygen permeability of the prepared novel SDC–PBCO membrane is mainly attributed to both the larger oxygen ion conducting phase content than the other composites and the electron network forming through the membrane. In addition, this novel dual-phase membrane structure decreases the enwrapped parts by each other
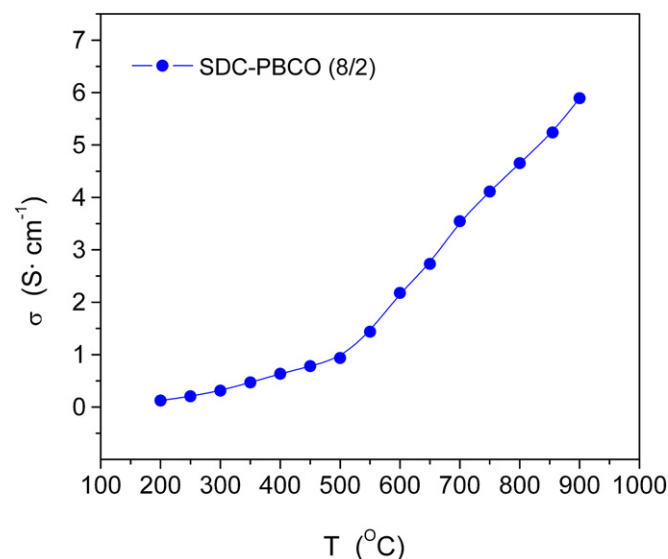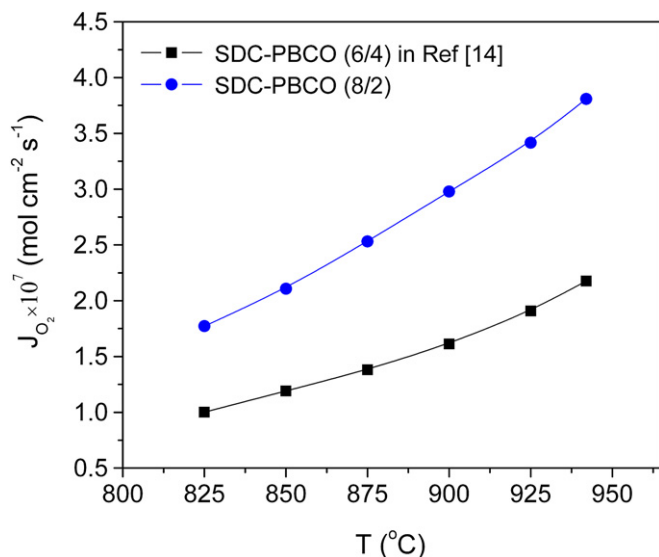
Fig. 3. Temperature dependence of electrical conductivity of the prepared SDC–PBCO composite.

Fig. 4. Oxygen permeation fluxes of SDC–PBCO (8/2) membrane prepared by coating route as a function of temperature. As comparison, the oxygen permeation fluxes of SDC–PBCO (6/4) [14] prepared by conventional ceramic route are included.

phase, which is also beneficial to the oxygen permeation process [15]. The permeation activation energy of this novel dual-phase membrane is about 72.4 ± 1.5 kJ mol^{-1}, which is close to the value of 69 kJ mol^{-1} obtained from oxygen ionic conductivity measurements on the SDC ceramic [16]. This provides evidence that the oxygen permeate process in the SDC–PBCO membrane is mainly limited by the transport of oxygen ions through the ionic conducting phase SDC.

4. Conclusions

A novel dual-phase membrane with 20 vol.% fiber-like $PrBaCo_2O_{5+\delta}$ dispersing in 80 vol.% $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ matrix was prepared by a coating strategy, coating the oxygen ionic conducting phase with nano-crystalline electronic conducting phase before pressing and sintering. The fiber-like PBCO phase in very low volume percentage forms percolative network, ensuring the electronic conducting channels through the dual-phase membrane. The high volume percentage of oxygen ion conducting phase SDC makes the SDC–PBCO membrane display very high oxygen permeability, 3.81×10^{-7} mol cm^{-2} s^{-1} at 940 °C. This strategy can be applied to other dual-phase membranes to improve the oxygen permeation performance.

References

[1] H.X. Luo, K. Efimov, H.Q. Jiang, A. Feldhoff, H.H. Wang, J. Caro, Angew. Chem. Int. Ed. 50 (2011) 759.
[2] J. Martynczuk, F. Liang, M. Arnold, V. Šepelák, A. Feldhoff, Chem. Mater. 21 (2009) 1586.
[3] A.F. Sammells, R.L. Cook, J.H. White, J.J. Osborne, R.C. MacDuff, Solid State Ionics 52 (1992) 111.
[4] V.V. Kharton, A.V. Kovalevsky, A.P. Viskup, F.M. Figueiredo, A.A. Yaremchenko, E.N. Naumovich, F.M.B. Marques, J. Electrochem. Soc. 147 (2000) 2814.
[5] M.B. Choi, S.Y. Jeon, H.J. Hwang, J.Y. Park, S.J. Song, Solid State Ionics 181 (2010) 1680.
[6] C. Wagner, W. Schottky, Z. Phys. Chem. B 11 (1930) 25.
[7] Z.L. Wu, M.L. Liu, Solid State Ionics 93 (1997) 65.
[8] J. Kim, Y.S. Lin, Ind. Eng. Chem. Res. 39 (2000) 2124.
[9] H.H. Wang, W.S. Yang, Y. Cong, X.F. Zhu, Y.S. Lin, J. Membr. Sci. 224 (2003) 107.
[10] T. Chen, H. Zhao, N. Xu, Y. Li, X. Lu, W. Ding, F. Li, J. Membr. Sci. 370 (2011) 158.
[11] K. Zhang, L. Ge, R. Ran, Z.P. Shao, S.M. Liu, Acta Mater. 56 (2008) 4876.
[12] H. Zhao, N. Xu, Y. Chen, W. Wei, N. Chen, W. Ding, X. Lu, F. Li, J. Phys. Chem. C 114 (2010) 17975.
[13] G. Kim, S. Wang, A.J. Jacobson, L. Reimus, P. Brodersen, C.A. Mims, J. Mater. Chem. 17 (2007) 2500.
[14] T. Chen, H. Zhao, Z. Xie, L. Feng, X. Lu, W. Ding, F. Li, Int. J. Hydrogen Energy 37 (2012) 5277.
[15] X.F. Zhu, W.S. Yang, AIChE J. 54 (2008) 665.
[16] D. Ding, B.B. Liu, Z.N. Zhu, S. Zhou, C.R. Xia, Solid State Ionics 179 (2008) 896.